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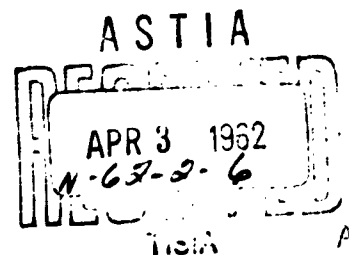
SECOND ANNUAL PROGRESS REPORT  
FOR THE  
OFFICE OF NAVAL RESEARCH  
CONTRACT NONR 3085(01)

ADDITION AND SUBSTITUTION  
PRODUCTS OF OXYGEN FLUORIDES

A. G. STRENG AND A. V. GROSSE

JANUARY 19, 1962

RESEARCH INSTITUTE



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**The Research Institute of Temple University  
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## INTRODUCTION

This is the Second Annual Report for the Office of Naval Research, Contract Nonr 3085(01). It covers the period from January 1 to December 31, 1961.

The research program was specified by the Research and Development Task Order and consists of the two following subjects:

- I. The synthesis and characterization of the oxygen fluorides.
- II. The synthesis and characterization of certain substitution and addition products of the oxygen fluorides.



### SUMMARY

A new type of highly colored deep-violet addition compounds of dioxygen difluoride has been obtained. These compounds are formed by addition to  $\text{ClF}$ ,  $\text{BrF}_3$  and  $\text{SF}_4$ , under mild reaction conditions. They have a remarkable oxidizing power, even at very low temperatures.

The analogous fluorides of the other elements adjoining oxygen and fluorine in the Periodic System, namely,  $\text{N}_2\text{F}_4$ ,  $\text{PF}_3$ ,  $\text{SiF}_4$ ,  $\text{CF}_4$  and  $\text{IF}_5$ , did not form addition compounds of this type.

The  $\text{O}_2\text{F}_2 + \text{ClF}$  reaction was studied extensively. Various combinations of the factors influencing the synthesis were investigated, and the yield of the violet addition product was raised to 81% of the theoretical value.

The investigation of the properties of the violet compound, the elementary composition of which was found to be  $\text{O}_2\text{ClF}_3$ , showed that the solid violet compound, contaminated only by  $\text{ClF}_3$ , is stable at  $195^\circ\text{K}$ . At this temperature it was kept for over 9 months without any noticeable decomposition. The compound is soluble in liquid  $\text{ClF}_3$ ,  $\text{ClF}$ ,  $\text{O}_2\text{F}_2$  and  $\text{HF}$ , at  $125\text{--}190^\circ\text{K}$ ., but is insoluble in liquid  $\text{O}_2$ ,  $\text{O}_3$ ,  $\text{ClO}_3\text{F}$ ,  $\text{C}_3\text{F}_8$ ,  $\text{NF}_3$ ,  $\text{CCl}_2\text{F}_2$  and  $\text{CClF}_3$  in the range of  $90\text{--}160^\circ\text{K}$ . The solutions are less stable than the solid compound. The measurements of the electrical conductivity of a solution of the violet compound in anhydrous  $\text{HF}$  at  $-78^\circ\text{C}$ . showed that  $\text{O}_2\text{ClF}_3$  is not an electrolyte.

The study of the reactivity of the violet compound at low temperatures showed its extremely high oxidizing power. The compound reacts vigorously with ammonia, ethane and ethylene, even at 120-160°K. There was no reaction, however, with liquid methane at 90°K.; with gaseous methane at 150°K.; and with gaseous hydrogen at 120°K. under a pressure of 100 mm. Hg.

The violet addition product was synthesized also from ClF<sub>3</sub> and O<sub>2</sub> at 195°K. under pressure, by irradiation with ultra-violet light. The preliminary data on the visible absorption spectrum of this compound were obtained.

The decomposition of a solution of O<sub>2</sub>ClF<sub>3</sub> in anhydrous HF led, under some conditions, to the formation of a blue compound or compounds. The nature of these compounds was not established.

The flow diagram and the description of the methods of preparation of O<sub>2</sub>F<sub>2</sub> and O<sub>3</sub>F<sub>2</sub> are given.

# I. A NEW TYPE OF HIGHLY COLORED ADDITION PRODUCTS OF DIOXYGEN DIFLUORIDE

The reactions of oxygen fluorides with various lower fluorides of the elements close to oxygen and fluorine in the Periodic System were studied. It was found that at low temperatures, i.e. 110-140°K., dioxygen difluoride,  $O_2F_2$ , adds chlorine monofluoride,  $ClF$ , forming a highly colored, purple to violet, addition compound. The elementary formula of this compound is  $O_2ClF_3$ . This is a new type of compound with remarkable oxidizing properties.

Bromine trifluoride,  $BrF_3$ , and sulfur tetrafluoride,  $SF_4$ , also form, under very mild conditions, highly colored brown-to-violet addition products.

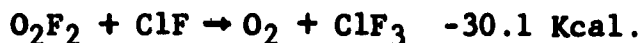
The fluorides of the other elements close to oxygen and fluorine in the Periodic System, namely, nitrogen, phosphorus, carbon and silicon do not form the violet addition compounds. Phosphorus trifluoride,  $PF_3$ , combines with  $O_2F_2$ , forming  $(POF_3)_n$  and  $PF_5$ . The  $POF_3$  is produced in the form of an interesting polymer which depolymerizes at higher temperatures to gaseous  $POF_3$ . Tetrafluorohydrazine,  $N_2F_4$ , reacts, giving  $O_2$  and  $NF_3$ . Carbon tetrafluoride,  $CF_4$ , and silicon tetrafluoride,  $SiF_4$ , do not react, as was expected, in view of their saturated nature. Iodine pentafluoride,  $IF_5$ , does not react at low temperatures but under more drastic conditions will probably form iodine heptafluoride,  $IF_7$ .

## II. THE $O_2F_2 + ClF$ REACTION. FORMATION OF $O_2ClF_3$

### A. Reaction Conditions

At  $90^\circ K.$ , solid dioxygen difluoride (m.p.  $109.7^\circ K.$ ) and solid chlorine monofluoride (m.p.  $119^\circ K.$ ) do not react when  $ClF$  is condensed on a thin solidified layer of  $O_2F_2$ .

Gaseous  $O_2F_2$ , on the other hand, at about  $195^\circ K.$ , reacts with  $ClF$  directly to give oxygen gas and  $ClF_3$ , without the formation of intermediate compounds. The reaction proceeds in accordance with the equation:



At temperatures of about  $110-140^\circ K.$ , however,  $O_2F_2$  reacts with  $ClF$ , forming a deep violet intermediate addition compound,  $O_2ClF_3$ . The formation of the violet compound is usually accompanied by the evolution of gaseous oxygen and fluorine in varying ratios. At temperatures above  $140^\circ K.$  the reaction proceeds violently. The  $ClF$  abstracts the fluorine from  $O_2F_2$  according to equation (1). If the addition of  $ClF$  is too rapid, some of the  $O_2F_2$  is decomposed to  $O_2$  and  $F_2$ .

At more moderate temperatures ( $110-140^\circ K.$ ) and with a slow addition of  $ClF$ , three reactions take place simultaneously in varying proportions.

The formation of the violet addition product:



The decomposition of the violet compound either at the time of formation or when the temperature is raised:



and the thermal decomposition of  $\text{O}_2\text{F}_2$ :

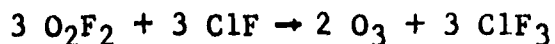


The extent of each reaction can be readily determined analytically, since reactions (2) and (3) produce gaseous oxygen and reaction (3), produces, in addition, free fluorine. The oxygen can be determined by standard Orsat analysis or other known methods; the fluorine by Hg-burette absorption; and the chlorine trifluoride by freezing it out (m.p. 190°K.) and checking its purity by vapor-pressure measurement, infrared spectrum or melting point.

Reaction (1) is difficult to control. Much effort was exerted to find the conditions necessary to minimize reactions (2) and (3); i.e., to increase the yield of the violet product.

Since the violet reaction product is energy rich, it decomposes rapidly if the reaction proceeds too violently or even under mild conditions, if impurities are present. In the presence of traces of water, nitrogen oxides or nitrogen oxyfluorides, the violet compound decomposes quickly or does not form.

In view of the intense color it was at first thought that ozone was formed, possibly following the equation:



Although ozone is deep blue and the reaction product violet-blue, ozone and liquid  $\text{O}_2\text{F}_2$  form a violet-blue solution.

It was found, however, that  $\text{O}_3$  does not dissolve in  $\text{ClF}_3$  and does not form an addition product with it. In the absence of  $\text{O}_2\text{F}_2$  and in the presence of  $\text{ClF}_3$ , ozone, as expected, retains its characteristic deep blue color. Ozone can be isolated easily from such a mixture by two methods: (1) by extraction with liquid  $\text{O}_2$ , which immediately gives a deep blue solution, while  $\text{ClF}_3$  remains practically insoluble, or (2) by high-vacuum distillation. At a total pressure of  $12\mu$  and at a temperature of  $158^\circ\text{K}$ ., the violet compound does not distil. Ozone, on the other hand, has a vapor pressure of 600 mm. at  $158^\circ\text{K}$ . and would readily distil.

The violet reaction product may be prepared simply by adding pure  $\text{ClF}$  to pure  $\text{O}_2\text{F}_2$ . The dioxygen difluoride is condensed in a reaction tube cooled in a liquid-oxygen bath, the  $\text{ClF}$  is added and the tube is warmed slowly. In the temperature range of about  $110$  to  $140^\circ\text{K}$ ., these compounds react, forming, together with other compounds, the intense violet addition product, which has strong oxidizing properties. The most favorable temperature is  $119^\circ\text{K}$ ., the melting point of  $\text{ClF}$ .

The yield of the violet compound depends upon the rate of addition of ClF, temperature, area and uniformity of distribution of O<sub>2</sub>F<sub>2</sub>.

The three reactions mentioned previously take place simultaneously. The optimum yield attained was about 50%, based on reaction (1), although in most cases the yield was very much smaller.

The simplest way to increase the yield is to dilute the reagents. Freon 13 (CClF<sub>3</sub>) was found to be a solvent for O<sub>2</sub>F<sub>2</sub> at about 130°. When gaseous ClF diluted with helium is bubbled through a solution of O<sub>2</sub>F<sub>2</sub> in Freon 13, cooled to 130-140°K., the reaction between O<sub>2</sub>F<sub>2</sub> and ClF proceeds in most cases without gas evolution; i.e., without decomposition of the violet compound into O<sub>2</sub> and ClF<sub>3</sub>, according to reaction (2), or without decomposition of O<sub>2</sub>F<sub>2</sub> into O<sub>2</sub> and F<sub>2</sub>, as in reaction (3). It was found, however, that in the presence of Freon 13, the thermal stability of the violet compound is substantially decreased. The violet compound is not soluble in Freon 13; it precipitates to the bottom of the reaction vessel and decomposes with considerable velocity at about 195°K. It may be that impurities in Freon 13 cause this decomposition.

There was no formation of a violet compound at all when Freon 12 (CCl<sub>2</sub>F<sub>2</sub>) was used as the solvent for O<sub>2</sub>F<sub>2</sub>. The synthesis

was attempted with a 6.3 wt.%  $O_2F_2$  solution in Freon 12. The solution was cooled to  $90^\circ K.$ ,  $ClF$  was added and the tube was slowly warmed up. The reaction between  $O_2F_2$  and  $ClF$  started at about  $130^\circ K.$ , but without the formation of a violet product.

The use of perchloryl fluoride as the solvent in the reaction between  $O_2F_2$  and  $ClF$  did not increase the yield of the violet compound but did serve to lower its stability. A 14.0 wt.%  $O_2F_2$  solution in  $ClO_3F$  was used. The solution was cooled to  $90^\circ K.$  and small portions of  $ClF$  gas were added. After each addition, the reaction vessel was warmed to  $125^\circ K.$  A slow reaction occurred, with the formation of a comparatively large amount of  $ClF_3$  and a comparatively small amount of the violet product. Both these products are insoluble in  $ClO_3F$  at  $125^\circ K.$  and collect on the bottom of the vessel. The vessel was then cooled again to  $90^\circ K.$  and a new portion of  $ClF$  was added. When all the  $O_2F_2$  was consumed, the reaction vessel was slowly warmed to  $190^\circ K.$  At this temperature,  $ClF_3$  dissolves completely in  $ClO_3F$  and the violet compound remains on the bottom in the form of dark violet flakes. The yield of the violet compound was much smaller than that obtained in the reaction between pure  $O_2F_2$  and  $ClF$ . At about  $195^\circ K.$  the violet compound decomposed completely.

Anhydrous hydrogen fluoride,  $HF$ , is also a good solvent for both  $O_2F_2$  and the violet compound. At its melting point,  $190^\circ K.$ , hydrogen fluoride dissolves about 23 mole %  $O_2ClF_3$ , forming a deep



violet solution. A difficulty arises, however, from the fact that the solution of the violet compound in HF is stable at 190-195°K., only under an oxygen pressure of about two atmospheres. For this reason the removal of HF and the isolation of the violet compound are complicated.

The attempts to lower the melting point of HF by the addition of  $\text{KF}^1$  and thereby to increase the stability of the solutions of the violet compound, gave no improvement. On the contrary, in the presence of KF the solutions of the violet compound in HF lost their color much faster than normally, most probably owing to the formation of  $\text{K}(\text{ClF}_4)$ .

Perfluoropropane,  $\text{C}_3\text{F}_8$  (m.p. 90°K., b.p. 235°K.), was also investigated as a diluent for the  $\text{O}_2\text{F}_2 + \text{ClF}$  reaction. It dissolves over 33 wt.% ClF at 150°K. and mixes homogeneously with it at 160°K. The solubility of  $\text{O}_2\text{F}_2$  in  $\text{C}_3\text{F}_8$ , however, is very low.

Perfluoropropane used as a diluent increased the yield of the violet compound up to 81% of theory. The violet compound and  $\text{ClF}_3$  are, however, not soluble in  $\text{C}_3\text{F}_8$ . The stability of the violet product in the presence of  $\text{C}_3\text{F}_8$  was found to be low.

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(1) Cady, G. H., J. Am. Chem. Soc., 56, 1431 (1934).

### B. Solvents for the Reagents and the Reaction Products

The effort is continuing to find a suitable solvent for the reagents,  $O_2F_2$  and  $ClF$ , and for the reaction products, in order to facilitate the isolation of the pure violet compound.

Hildebrand's generally useful concept of solubility parameters<sup>2</sup> does not always predict correctly the solubility behavior of liquefied gases at low temperatures.<sup>3</sup> It was, therefore, necessary to obtain miscibility and solubility information experimentally.

The substances tested and the results obtained to date are as follows:

	<u>Mixes homogeneously with:</u>	<u>Forms two practically insoluble layers with:</u>
$O_2F_2$ :	$O_3F_2$ at $116^\circ K$ . $CCl_2F_2$ 116 $CClF_3$ 116 $CO_3F$ 127 $ClF_3$ 180 $NO_2F$ 195	$N_2$ at $77^\circ K$ . $F_2$ 77 $CF_4$ 90 $O_2$ 90 $NF_3$ 130 $C_3F_8$ 140 $N_2F_4$ 130
$ClF$ :	$CO_3F$ at $160^\circ K$ . $C_3F_8$ 160	$O_3F_2$ at $90^\circ K$ . $NF_3$ 150 $ClF_3$ 174 $HF$ 173
$ClF_3$ :	$O_2F_2$ at $180^\circ K$ . $ClO_3F$ 195 $HF$ 195	$O_3F_2$ at $90^\circ K$ . $NF_3$ 140 $ClF$ 174 $CCl_2F_2$ 125 $CClF_3$ 190 $C_3F_8$ 235

(2) Hildebrand, J. H., and Scott, R. L., "The Solubility of Non-electrolytes," 3rd Ed. Reinhold, New York, 1950.

(3) Streng, A. G., and Grosse, A. V., "The Different Solubility Behavior of the Isothermic Liquids  $CO$  and  $N_2$  in Liquid Ozone," J. Inorg. & Nucl. Chem., 9, 315 (1959).

In the course of these investigations it was found also that:

- 1)  $O_2F_2$  dissolves about 20 wt.% of  $SiF_4$  at  $150^\circ K$ .  
and about 11 wt.% of HF at  $186^\circ K$ .
- 2) HF dissolves at least 6.6 mole % ClF at  $190^\circ K$ .  
and about 5.8 wt.%  $O_2F_2$  at  $176^\circ K$ . and 11.6 wt.%  
 $O_2F_2$  at  $186^\circ K$ .
- 3) FC-15 ( $C_8F_{16}O$ ) dissolves about 3 wt.%  $ClF_3$  at  $195^\circ K$ .
- 4)  $C_3F_8$  dissolves some  $O_2F_2$  at  $130^\circ K$ .
- 5)  $N_2F_4$  dissolves some  $O_2F_2$  at  $140^\circ K$ .

#### C. Formation of an Unknown Blue Compound or Compounds

If the violet compound is warmed up to about  $140^\circ K$ . in the presence of ClF and  $ClF_3$ , it changes into a greenish-blue compound, which exists only over a very narrow temperature range. The greenish-blue compound dissolves in ClF at about  $125-130^\circ K$ ., to form a greenish-blue solution, but the color disappears in about three to five minutes. Probably another blue compound was formed while pumping off the oxygen from a violet solution of  $O_2ClF_3$  in anhydrous HF at  $190-195^\circ K$ . The solution changed color and became deep blue like the color of ozone. The question might well be raised whether in the decomposition of  $O_2ClF_3$  the oxygen is liberated as  $O_3$  or whether a new type of compound is formed which has a color similar to that of ozone. This possibility will be checked later by

determining the visible absorption spectrum of the solution.

It is of interest to mention here that over 3.5 wt.% of ozone dissolves in HF at 195°K. and at pressures less than one atmosphere to form a solution similar in appearance to the one described above.

D. Synthesis of the Violet Compound Directly  
From O<sub>2</sub> and ClF<sub>3</sub> Under the Influence  
of Ultraviolet Light

The discovery that oxygen pressure has an important effect on the stability of the violet compound dissolved in HF, led us to the experiment described below.

Pure ClF<sub>3</sub> was placed in a quartz tube surrounded by dry ice, i.e., at 195°K., and irradiated with ultraviolet light, principally at 2537 Ångstrom units with an intensity of 7 milliwatts/cm<sup>2</sup>. Under a pressure of two atmospheres of oxygen a violet compound was produced after only a few seconds irradiation; the color increased appreciably with time. On the other hand, if the pressure of the oxygen was only 15 mm. the violet compound was not formed. A check experiment on pure ClF<sub>3</sub> in the absence of oxygen showed no change in color. Thus, at the present time we have a reversible reaction for the formation of the violet compound from the simple, commercially available materials, O<sub>2</sub> and ClF<sub>3</sub>, merely by changing the pressure of the oxygen.

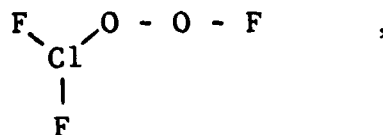
### III. THE PROPERTIES OF THE VIOLET $O_2F_2 + ClF$ ADDITION PRODUCT

#### A. General

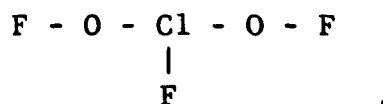
From classical theories of structure of inorganic chemistry, and a knowledge of the structure of  $O_2F_2$  certain simple structures of the new compound may be postulated. The structure of  $O_2F_2$  has been determined to be:



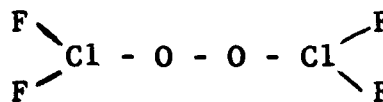
Since the chlorine in  $ClF$  is monovalent and can be converted to trivalent chlorine, the simplest assumption is that the addition of  $ClF$  to  $F - O - O - F$  takes place either (a) across the  $O - F$  bond, leading to the compound:



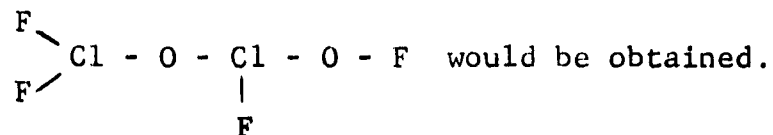
or (b) across the  $O - O$  bond, leading to the compound:



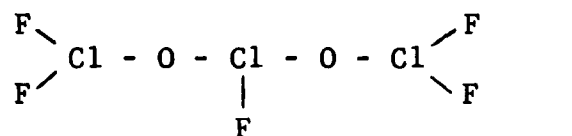
In case (a), the addition of a second molecule of  $ClF$  would lead to the compound:



In the less likely case of addition of the second molecule across the O - O bond the isomeric compound



The latter compound could also add a third molecule of ClF leading to the compound:



Either of the alternatives (a) and (b) is possible, because the bond strengths F - O - and - O - O - are not very different. They are estimated to be 61 Kcal. for - O - O - and 50 Kcal for F - O -, assuming a chain structure in O<sub>2</sub>F<sub>2</sub>.

The following properties of the compound have been determined so far:

The color is close to that of a 0.1% aqueous solution of the intense violet dye methyl violet. It is solid at 195°K. and in the absence of impurities can be kept at this temperature for months without noticeable decomposition. The thermal stability of the compound depends on the presence of catalysts or inhibitors of decomposition. It was found that if the original O<sub>2</sub>F<sub>2</sub> contains nitrogen compounds

such as NOF, NO<sub>2</sub>F, or NO<sub>2</sub> or other oxides of nitrogen, the decomposition of the violet compound is catalyzed so that the yields are very poor and the thermal stability is low.

The vapor pressure of the violet reaction product at 158°K. is below 12 microns.

The following observations were also made: If the O<sub>2</sub>F<sub>2</sub> + ClF reaction is carried out with an excess of ClF or in the presence of ClO<sub>3</sub>F or Freons 12 and 13 as diluents, the yield of the violet compound is low.

The violet compound is stable at temperatures up to 195°K. and has been kept at this temperature for 9 months. In general it was found that the stability of dry solid violet product is much higher than its stability in the dissolved state.

It was noted that the violet compound does not distill at 160°K. even at a pressure of 12 microns. It was found, however, that under these conditions it dissociates into O<sub>2</sub>F<sub>2</sub> and ClF, which were recovered in a liquid-nitrogen trap. If these dissociation products are warmed to about 130°K. the deep violet compound forms again.

#### B. Solubility

.

The search for a suitable solvent for the O<sub>2</sub>F<sub>2</sub> + ClF violet reaction product continues. The following substances have been

tested, and the results obtained to date are listed below:

The violet compound is soluble in:

liquid ClF	at 125°K.
" O <sub>2</sub> F <sub>2</sub>	at 140
" ClF <sub>3</sub>	at 190
" HF	at 190

The stability of all these solvents is lower than the stability of the violet compound in the solid state.

The violet compound is not soluble in:

liquid O <sub>2</sub>	at 90°K.
" O <sub>3</sub>	at 90
" ClO <sub>3</sub> F	at 135
" C <sub>3</sub> F <sub>8</sub>	at 140
" NF <sub>3</sub>	at 150
" CCl <sub>2</sub> F <sub>2</sub>	at 160
" CClF <sub>3</sub>	at 160

### C. Conductivity

The electrolytic conductivity of a solution of the violet compound in HF was measured by using a Wheatstone bridge\* and a specially made Teflon cell with platinum electrodes.

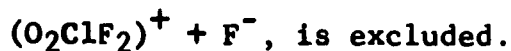
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(\*) Impedance bridge, Type 650A of the General Radio Co., Cambridge, Mass.



A 0.5-molar solution of  $\text{O}_2\text{ClF}_3$  in HF was investigated at 195°K. The anhydrous HF had a specific conductivity of  $3.57 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ . The conductivity of the violet solution was  $3.33 \times 10^{-3}$  and changed upon standing for an hour to  $3.57 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ . After this change, the violet compound was permitted to decompose by pumping off the oxygen, and the residual clean colorless solution of  $\text{ClF}_3$  in HF had a conductivity of  $3.57 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ . The best data on the specific conductivity of pure HF indicate that our HF contained traces of water in the amount of 2 mg. per liter.<sup>4</sup>

It is obvious that our violet compound does not increase the specific conductivity of anhydrous HF and is consequently not an electrolyte. In contrast, a 0.5-molar solution of a typical electrolyte, namely, KF in HF, has a specific conductivity of  $86.0 \text{ ohm}^{-1} \text{ cm}^{-1}$ . Thus, a similar concentration of potassium fluoride conducts the current approximately 25,000 times better than does our violet compound. The possibility that our violet compound,  $\text{O}_2\text{ClF}_3$ , might be ionic or salt like, dissociating for example into the ions,




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(4) Simons, J. H., "Fluorine Chemistry," Vol. 1, Academic Press, Inc., N. Y., 1950, p. 240.

#### D. Visible Spectrum

It was previously reported that the violet compound is also formed when liquid  $\text{ClF}_3$  (in the presence of oxygen at 195°K.) is irradiated with ultraviolet light. The visible spectrum of this compound was taken.

The violet compound was prepared for this investigation directly in a specially made silica-glass spectroscopic cell. The cell was filled with  $\text{ClF}_3$  to about two-thirds of its capacity and gaseous  $\text{O}_2$  (two atmospheres pressure) was added. The cell was then exposed for 15-20 min. at 195°K. to ultraviolet light of 2537Å units and an intensity of 7 milliwatts/cm<sup>2</sup>.

The spectrum was taken on a Beckman spectrophotometer, Model DU, fitted with a special cell compartment for measurements at low temperatures.<sup>3</sup>

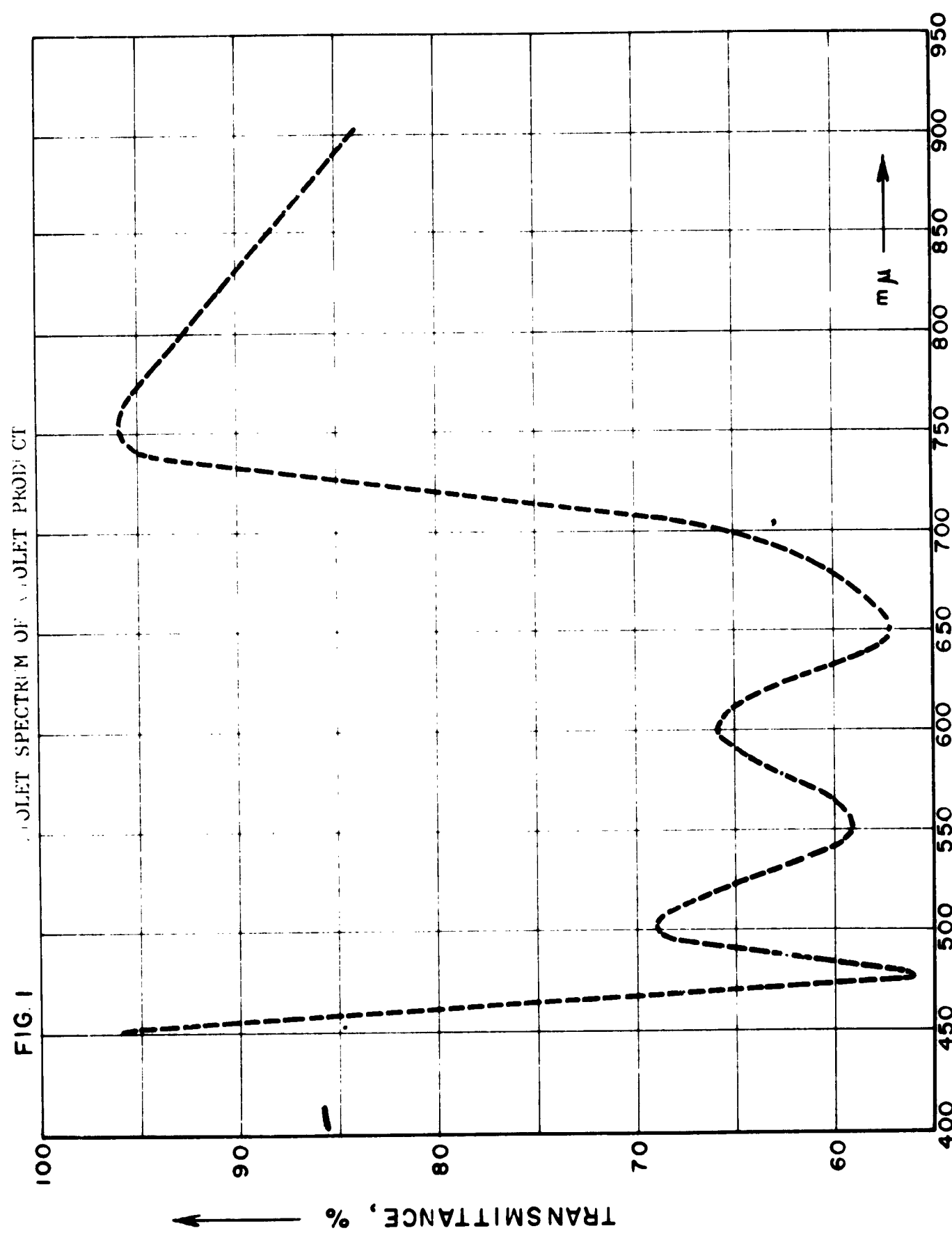
The preliminary data obtained are given in Table I and Fig. 1.

TABLE I

Preliminary Data on Visible Spectrum of  
Violet Compound Formed by  $\text{ClF}_3 + \text{O}_2$   
Under Ultra-Violet Light at 195°K.

<u>Wave length,</u> <u>m</u>	<u>Transmittance,</u> <u>%</u>	<u>Estimated molar</u> <u>extinction coefficient,</u> <u><math>\text{cm}^{-1} \text{ mole}^{-1} \text{ lit.}</math></u>
450	96	--
475	56	50
500	69	--
550	59	46
600	66	--
650	57	49
700	67	--
750	96	--
850	88	--
900	84	--

The concentration of the solution used was estimated to be about  
0.005 mole/lit.



#### IV. CHEMICAL REACTIONS OF $O_2ClF_3$ AT LOW TEMPERATURES

It was found that dioxygen monochlorotrifluoride,  $O_2ClF_3$ , is highly reactive at low temperatures towards ammonia and various hydrocarbons. In this respect it is similar to the highly reactive ozone, which was found to react even at 150-160°K. with ammonia.<sup>5</sup> Usually no chemical reactions take place at a temperature range of 100-150°K. outside of exceptionally reactive systems; for example, free atoms or radicals, as has been strikingly demonstrated by Dr. H. Broida and his associates at the National Bureau of Standards.

Since  $O_2ClF_3$  is of interest as a potential oxidizer, it was of importance to study its reactions with various hydrides.

##### A. Reaction with Ammonia

It was established in preliminary experiments, that gaseous ammonia entering a reaction vessel which contains the deep-violet  $O_2ClF_3$ , at a temperature of 90°K., reacts violently with a flash, forming some white solids and some nitrogen-containing gases, while the violet color disappears.

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(5) Grosse, A. V., and Streng, A. G., Technical Note No. 4, Contract No. AF 18(600)-1475, Project No. 7-7968, the Research Institute of Temple University, August 1, 1957.

If the ammonia is condensed first in the upper part of the reaction tube cooled to  $90^{\circ}\text{K}$ ., then the reaction proceeds slowly as the vessel is warmed up to  $150\text{-}160^{\circ}\text{K}$ . Ammonia has a vapor pressure of about 1 mm. at  $160^{\circ}\text{K}$ . and therefore evaporates slowly and reacts as a gas with the solid violet compound. Under these conditions the reaction proceeds smoothly without any gas evolution. The violet color disappears and a white solid is formed.

Ammonium fluoride and other ammonium salts, HF, HCL, and the oxy-acids of chlorine (either free or as ammonium salts) were identified among the reaction products.

Hydrogen fluoride was identified by vacuum distillation, formation of NaF. HF and titration. Hydrogen chloride was identified through formation of silver chloride. Ammonia was determined quantitatively by Kjeldahl's method. The oxynitrogen acids or oxychlorine acids were identified qualitatively by Lunge's reagent. Anions of the oxychlorine acids, i.e., chlorite, chlorate or perchlorate, were identified by reduction with zinc to chloride ion.

In one experiment 0.25 g.  $\text{O}_2\text{ClF}_3$  was reacted with about 0.10 g. of ammonia. 52 mg. of  $\text{NH}_3$  was found in the reaction product together with about 3 mg. of  $\text{N}_2$  (gas). Thus, about one-half of the ammonia added formed ammonium salts. This mixture of ammonium salts and oxidizers is potentially dangerous and can detonate!

### B. Reaction with Methane

Dioxygen monochlorotrifluoride does not react with an excess of liquid methane at 90°K. It also does not react with gaseous methane at a pressure of 100 mm. Hg at 150°K. During one hour there was neither a decrease in pressure nor a disappearance of the violet color.

### C. Reaction with Ethane

In contrast with the observations in the case of methane, ethane, when admitted to the violet compound at a temperature of 140°K., reacted immediately. The violet color disappeared and white solids were formed but no gas was evolved. That is, there was no formation of O<sub>2</sub>, F<sub>2</sub> or CO.

Hydrogen fluoride was identified in the reaction products as was ClF<sub>3</sub>, which was present as a contaminant in the original O<sub>2</sub>ClF<sub>3</sub>.

### D. Reaction with Ethylene

The reaction vessel containing 1.39 g. of O<sub>2</sub>ClF<sub>3</sub> was cooled to 120°K. and ethylene gas was introduced (ethylene has a vapor pressure of about 1.0 mm. Hg at 120°K.) in portions of about 5 mg. at a rate of about 1 mg. per sec. After an interruption of one to two minutes, new portions were added.

Under those conditions ethylene reacted immediately, causing decolorization of the violet compound and formation of the white solid products, while no measurable gas evolution, i.e. no formation of  $O_2$ ,  $F_2$  or  $CO$ , took place.

On one occasion when ethylene was added at a higher rate, the reaction proceeded with a flame which extinguished itself as soon as the ethylene flow was stopped. A total of 0.179 g. of ethylene was added to 1.3 g. of  $O_2ClF_3$ ; the temperature of the bath after this addition was slowly raised at the rate of  $1-1\frac{1}{2}^\circ/\text{min}$ . No gas evolution was noticed up to  $140^\circ K$ . At  $140^\circ K$ . a violent explosion took place, shattering the reaction vessel and a large part of the reaction system. Evidently, intermediate or partly oxidized products were formed.

In all reactions of  $O_2ClF_3$  with hydrogen-containing substances,  $HF$  is the most likely reaction product. Carbonyl fluoride,  $COF_2$  and other intermediate oxyfluorides, for example, oxalyl fluoride,  $C_2O_2F_2$ , may be formed. In view of the violent explosion which took place, it is also likely that some C-H containing compounds were present.

#### E. Reaction with Hydrogen

During one hour at  $90-120^\circ K$ . there was no reaction between  $O_2ClF_3$  and hydrogen gas at a pressure of 100 mm. Hg. Any reaction



would be easily noticeable by disappearance or change of the violet color or a decrease in the pressure of hydrogen.

The nonreactivity of  $\text{O}_2\text{ClF}_3$  with hydrogen and methane parallels the chemical properties of ozone. We have shown earlier that pure (100%) ozone can be mixed at  $-78^\circ\text{C}$ . and even at room temperature with hydrogen and methane without reaction.<sup>6,7</sup> (The mixture  $1.5 \text{ CH}_4 + 2\text{O}_3$ , at 804 mm. Hg., showed at  $+21^\circ\text{C}$ . a pressure increase of 26 mm. Hg. on standing for 1.0 hour).

From the present preliminary evidence it is likely that  $\text{O}_2\text{ClF}_3$  will be more reactive than ozone at low temperatures.

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(6) Streng, A. G., and Grosse, A. V., J. Am. Chem. Soc., **79**, 3996 (1957).

(7) Streng, A. G., and Grosse, A. V., "Advances in Chemistry Series," Vol. 21, page 40, Am. Chem. Soc., Washington, 1959

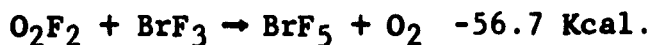
## V. REACTION OF $O_2F_2$ WITH $BrF_3$ AND $SF_4$

The lower fluorides of bromine and sulfur,  $BrF_3$  and  $SF_4$ , under very mild conditions may also form highly colored addition products with  $O_2F_2$ , although the compounds so far made seem to have only a transitory existence. The reactions are not always reproducible. Silicon tetrafluoride,  $SiF_4$ , interferes with the formation of the addition products.

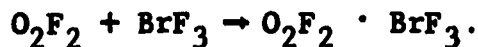
### A. The $O_2F_2$ + $BrF_3$ Reaction

The bromine analog of  $ClF$ , bromine trifluoride,  $BrF_3$ , also reacts with  $O_2F_2$ .

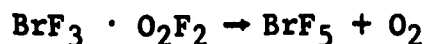
If liquid  $BrF_3$  cooled to its melting point,  $282^\circ K.$ , is dropped onto solid  $O_2F_2$  cooled to  $90^\circ K.$ , a spontaneous reaction occurs with evolution of heat and gas. Analysis of the reaction products showed that the reaction proceeds in accordance with the equation:



Under milder conditions, a brown-violet compound may be formed. The reaction proceeds, analogously to the  $ClF$  reaction, according to the equation:



Bromine trifluoride was condensed on the walls of the reaction vessel at 90°K. A thin layer of O<sub>2</sub>F<sub>2</sub> was then condensed on the BrF<sub>3</sub> surface. The bath temperature was slowly raised and at about 130°K. the reaction between BrF<sub>3</sub> and O<sub>2</sub>F<sub>2</sub> began, forming a violet-brown compound, with some gas evolution. Analysis showed that the gas evolved consisted mainly of oxygen (with a small amount of fluorine), which forms according to the reaction:

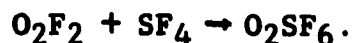


The colorless liquid reaction product was identified as BrF<sub>5</sub>. The small amount of F<sub>2</sub> gas formed is due to partial decomposition of O<sub>2</sub>F<sub>2</sub>.

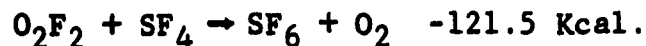
The yield of the violet-brown compound was about 80%. The compound began to decompose at 150°K. and decomposed completely at 170°K. to oxygen and BrF<sub>5</sub>.

#### B. The O<sub>2</sub>F<sub>2</sub> + SF<sub>4</sub> Reaction

The sulfur analog of ClF, sulfur tetrafluoride, SF<sub>4</sub>, can also form an intensely violet-colored compound. The difficultly reproducible reaction proceeds most likely in accordance with the equation:



Pure  $\text{O}_2\text{F}_2$  and  $\text{SF}_4$  react violently in accordance with the equation:



without the formation of an intermediate violet product. In an attempt to prevent a violent reaction both reactants were diluted with perchloryl fluoride. This solvent was used earlier in the  $\text{O}_2\text{F}_2 + \text{ClF}$  reaction.

The solubility of sulfur hexafluoride,  $\text{SF}_6$ , in  $\text{ClO}_3\text{F}$  at low temperatures was found to be much higher than the solubility of  $\text{ClF}_3$ , see Fig. 2. Therefore, the separation of an intermediate product would be comparatively easy.

It was found, however, that if both  $\text{O}_2\text{F}_2$  and  $\text{SF}_4$  are diluted with perchloryl fluoride, the intermediate violet product either forms only in very small amounts or does not form at all.

A 12.8 wt.%  $\text{O}_2\text{F}_2$  solution was used, for example. It was frozen at  $90^\circ\text{K}$ . and a gaseous  $\text{SF}_4\text{-ClO}_3\text{F}$  (1:1) mixture was added in small portions containing 20-100 mg. of  $\text{SF}_4$ . After the addition of each portion, the reaction vessel was warmed to  $130^\circ\text{K}$ .

Only traces of violet compound formed, which deposited on the walls of the reaction vessel above the  $\text{O}_2\text{F}_2\text{-ClO}_3\text{F}$  mixture. The formation of the violet compound took place only at temperature of  $90^\circ\text{-}116^\circ\text{K}$ . At  $130^\circ\text{K}$ . a slow visible reaction between  $\text{O}_2\text{F}_2$  and  $\text{SF}_4$  began with evolution of  $\text{O}_2$  gas and formation of  $\text{SF}_6$ .

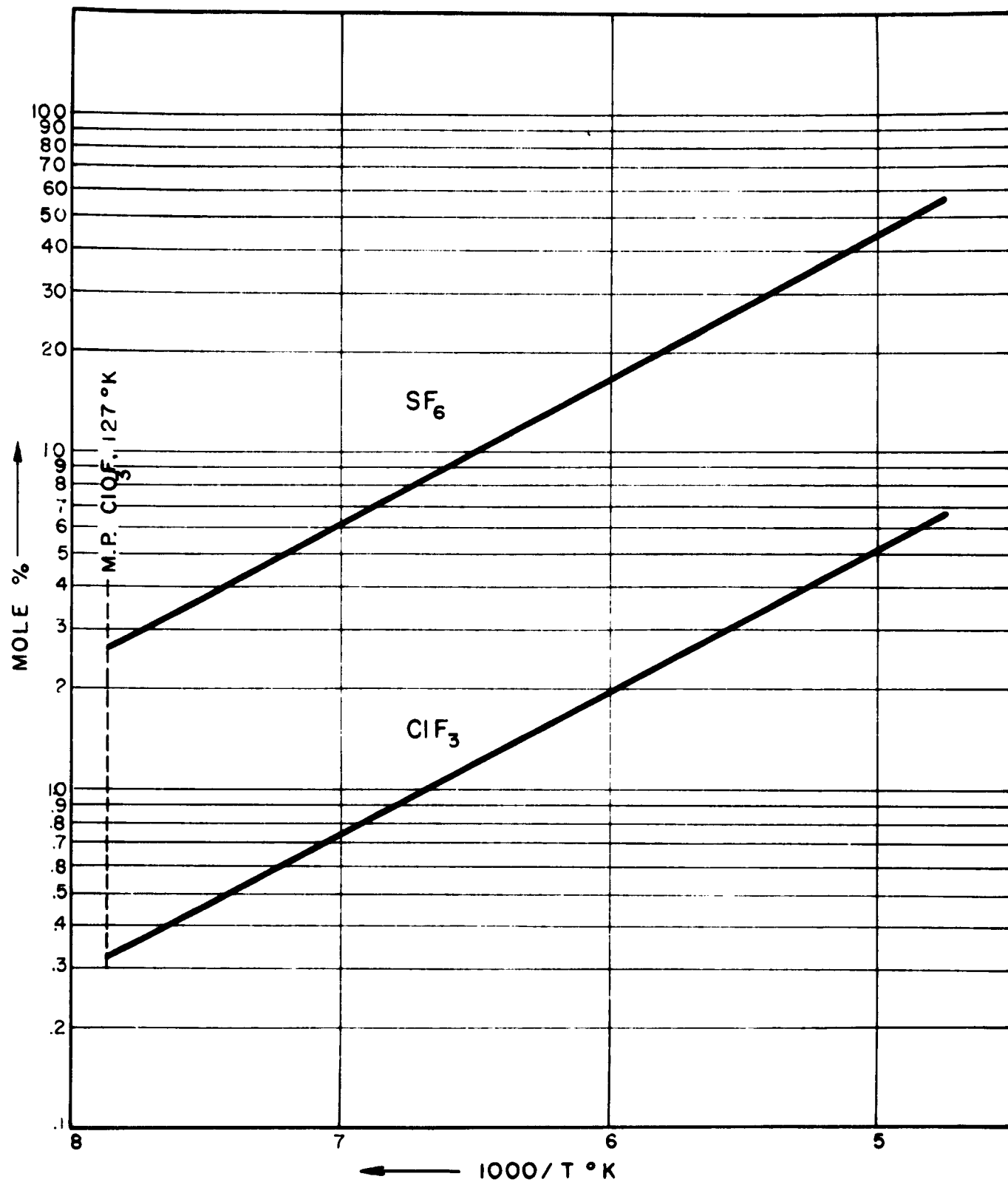


FIGURE 2.

SOLUBILITY OF  $\text{SF}_6$  AND  $\text{ClF}_3$  IN  $\text{CO}_2$

Further warming to 150°-170°K. increased the reaction rate and caused decomposition of the violet compound. Also decomposition of  $O_2F_2$  to  $O_2$  and  $F_2$  was noted.

Use of a smaller amount of diluent gave a larger quantity of the violet product, but the reaction was difficult to control.

Sulfur tetrafluoride diluted with  $ClO_3F$  was distilled into the reaction tube containing frozen  $O_2F_2$  at 90°K. Traces of a violet-purple compound formed immediately on the walls of the reaction vessel, even at 90°K. Most of the  $SF_4$  and  $ClO_3F$  condensed on the walls above the  $O_2F_2$ . The tube was then warmed above 125°K. At about 130°K. the  $SF_4$ - $ClO_3F$  mixture began to melt and flow down to the  $O_2F_2$ . More purple-violet compound formed and the reaction went out of control with an explosively violent evolution of gas and heat. The excess  $O_2F_2$  remained on the bottom of the shattered reaction tube.

#### C. Irradiation of $SF_4 + O_2$ with Ultraviolet Light

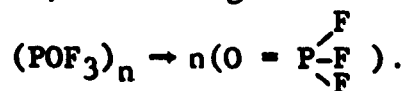
In contrast to  $ClF$ , sulfur tetrafluoride does not produce colored compounds with gaseous oxygen at two atmospheres pressure, when exposed to ultraviolet light. Sulfur tetrafluoride +  $O_2$  was irradiated under the conditions used for  $ClF_3 + O_2$ , in the temperature range of 90°-195°K. No violet compound was formed.

VI. CHEMICAL BEHAVIOR OF  $O_2F_2$  WITH FLUORIDES  
OF ELEMENTS CLOSE TO OXYGEN AND  
FLUORINE IN THE PERIODIC SYSTEM

A. The Reaction of  $O_2F_2$  with  $PF_3$

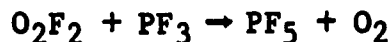
The phosphorus analog of  $ClF$ , namely the phosphorus tri-fluoride,  $PF_3$  (an analog in the same sense as  $BF_3$ ,  $SF_4$  and  $IF_5$ , i.e., in that all these compounds add two atoms of fluorine to form the highest fluoride of the element), does not form a colored addition compound with  $O_2F_2$ .

Dioxygen difluoride, however, does react with  $PF_3$ , forming oxygen and  $PF_5$ . At the same time some of the oxygen liberated reacts with  $PF_3$ , forming a solid, white compound at  $0^\circ C$ . The white compound is fairly stable at  $0^\circ C$ . This compound is the only solid reaction product; it is not the well known  $POF_3$ , which melts at  $233.4^\circ K$ . and boils at  $233.8^\circ K$ . but is an interesting polymer of  $POF_3$ . On standing at  $0^\circ C$ . or at room temperature, the polymer depolymerizes completely to  $POF_3$  (which was identified by its infrared spectrum) according to the equation:



Gaseous  $PF_3$  was introduced in small portions (15-50mg.) into a Pyrex glass reaction tube containing  $O_2F_2$  frozen at  $90^\circ K$ . The  $PF_3$  solidified on the walls above the  $O_2F_2$ . The tube was then warmed slowly to  $125^\circ K$ . Both  $O_2F_2$  and  $PF_3$  melted and reacted at

this temperature with gas evolution to form a white solid. If the amount of  $\text{PF}_3$  added in one portion was larger than 50 mg. or if the compounds were warmed quickly, the reaction proceeded with flame. The gas evolved was found to be oxygen. Phosphorus pentafluoride and polymeric  $\text{POF}_3$  were identified as the reaction products:



#### B. The Reaction of $\text{O}_2\text{F}_2$ with $\text{IF}_5$

In contrast to  $\text{BrF}_3$ , the analogous iodine compound,  $\text{IF}_5$ , does not form a colored compound. It was found that  $\text{O}_2\text{F}_2$  decomposes in the presence of  $\text{IF}_5$  to  $\text{O}_2$  and  $\text{F}_2$ , without the formation of  $\text{IF}_7$ . Under the same conditions both  $\text{ClF}$  and  $\text{BrF}_3$  formed violet addition compounds.

Liquid  $\text{IF}_5$  was distributed on the walls of a reaction vessel and frozen at  $90^\circ\text{K}$ . The equivalent amount of  $\text{O}_2\text{F}_2$  was then condensed upon the  $\text{IF}_5$  surface. The reaction vessel was then warmed slowly to  $195^\circ\text{K}$ . There was no reaction between  $\text{O}_2\text{F}_2$  and  $\text{IF}_5$  over the temperature range  $90^\circ$ - $195^\circ\text{K}$ . Only a slow decomposition of  $\text{O}_2\text{F}_2$  to  $\text{O}_2$  and  $\text{F}_2$  occurred.

#### C. The Reactions of $\text{O}_2\text{F}_2$ with $\text{SiF}_4$ and $\text{CF}_4$

Solid  $\text{SiF}_4$  (m.p.  $183^\circ\text{K}$ .) does not react with liquid  $\text{O}_2\text{F}_2$ .



Approximately 20%  $\text{SiF}_4$  is soluble in liquid  $\text{O}_2\text{F}_2$  at  $150^\circ\text{K}$ . without noticeable formation of addition compounds. At about  $195^\circ\text{K}$ .  $\text{O}_2\text{F}_2$  decomposes into  $\text{O}_2$  and  $\text{F}_2$ , while  $\text{SiF}_4$  remains unchanged.

A measured amount of  $\text{SiF}_4$  was added to a known amount of  $\text{O}_2\text{F}_2$  cooled in a reaction vessel to  $90^\circ\text{K}$ . The  $\text{O}_2\text{F}_2:\text{SiF}_4$  molar ratio was 1:0.4. The reaction vessel was warmed to  $120^\circ\text{K}$ . The  $\text{O}_2\text{F}_2$  melted and dissolved some  $\text{SiF}_4$ , but did not react. The temperature of the bath was then increased to  $150^\circ\text{K}$ . More  $\text{SiF}_4$  dissolved but no reaction occurred. After 2 hrs. at  $150^\circ\text{K}$ . the reagents were separated by distillation. Silicon tetrafluoride was collected in a U-tube and its purity was checked by infra-red spectroscopy and by melting point and vapor pressure measurements.  $\text{O}_2\text{F}_2$  was decomposed to  $\text{O}_2$  and  $\text{F}_2$  which were identified by standard procedures.

Similarly, carbon tetrafluoride,  $\text{CF}_4$ , does not react with  $\text{O}_2\text{F}_2$ .

#### D. The Reaction of $\text{O}_2\text{F}_2$ with $\text{N}_2\text{F}_4$

Dioxygen difluoride does not react with  $\text{NF}_3$  but does react with the lower fluoride of nitrogen, tetrafluorohydrazine,  $\text{N}_2\text{F}_4$ .

According to Johnson and Colburn<sup>8</sup> condensation of cold

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(8) Johnson, F. A., and Colburn, C. B., J. Am. Chem. Soc., **83**, 3043 (1961).

gaseous  $\text{N}_2\text{F}_4$  ( $-30^\circ\text{C}.$ ) at relatively high pressures, gives a water-white liquid. However, if the gas is condensed at elevated temperatures and low pressures, the liquid obtained has color varying from light blue to blue-black. The intensity of color is said to be a function of the concentration of  $\text{NF}_2$  radicals in the gas phase prior to condensation and is supposedly due to an "association compound."

Our experience with  $\text{N}_2\text{F}_4$  showed that upon distillation, either in Pyrex glass or in a Kel-F system, a violet compound is formed; it looks like the violet compound formed by the reaction between  $\text{O}_2\text{F}_2$  and  $\text{ClF}$  but it has different properties.

A series of experiments was performed to determine the nature of this compound before using  $\text{N}_2\text{F}_4$  for the reaction with  $\text{O}_2\text{F}_2$ . It was made clear that this violet compound is not of the same type as was obtained in the  $\text{O}_2\text{F}_2 + \text{ClF}$  reaction.

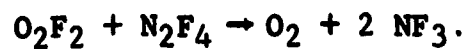
The violet compound formed by  $\text{N}_2\text{F}_4$  can be distilled from one vessel into another together with  $\text{N}_2\text{F}_4$  without decomposition, whereas our violet compound is nonvolatile.

About 0.6 g.  $\text{O}_2\text{F}_2$  was reacted in a Kel-F system with 1.4 g.  $\text{N}_2\text{F}_4$  at  $130-170^\circ\text{K}.$  A visible reaction started at  $170^\circ\text{K}.$  without the formation of any colored compounds.

The reaction products were  $\text{O}_2$  and  $\text{NF}_3$ . The  $\text{O}_2$  was

identified by pyrogallol absorbtion and  $\text{NF}_3$  as a colorless liquid in liquid  $\text{N}_2$  (b.p. =  $77^\circ\text{K}.$ ), while the original  $\text{N}_2\text{F}_4$  is a white solid with a melting point of  $110^\circ\text{K}.$

The most probable reaction is:



## VII. EXPERIMENTS IN A U-SHAPE ELECTRICAL-DISCHARGE TUBE

The preparation of  $O_2F_2$ ,  $O_3F_2$  and  $O_4F_2$  by an electrical-discharge method is best performed in specially designed vessels.\* Entirely different reaction products may form in reaction vessels of different sizes and shapes.

An electrical discharge was passed, for example, through a  $1.5O_2+F_2$  gas mixture (adequate for the preparation of  $O_3F_2$ ) in the U-shape electrical discharge tube shown in Fig. 3. The conditions were:  $T = 77\text{ K.}$ ,  $P = 12\text{-}17\text{mm. Hg.}$ ,  $V = 2000\text{-}2500\text{ v.}$ ,  $A = 20\text{-}30\text{ ma.}$  Under these conditions  $O_3F_2$  forms in the vessel recommended. But in the U-shape vessel, three quite different products were obtained: ozone, dioxygen difluoride and traces of a violet compound not yet investigated. The wall of the left side of the U-tube (the part where the  $O_2\text{-}F_2$  mixture enters) was covered with a deposit of  $O_2F_2$ . On the wall of the lower part of the right side a blue layer of ozone was formed, while on the wall of the upper part of the right side (above the ozone ring) a very small amount of a violet compound was deposited. Several mild explosions occurred in the gaseous phase during the operation owing, most probably, to the formation of ozone. This was never the case in the recommended type of reaction vessel.

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(\*) See Fig. A-2 and A-3 in the Appendix of this Report.

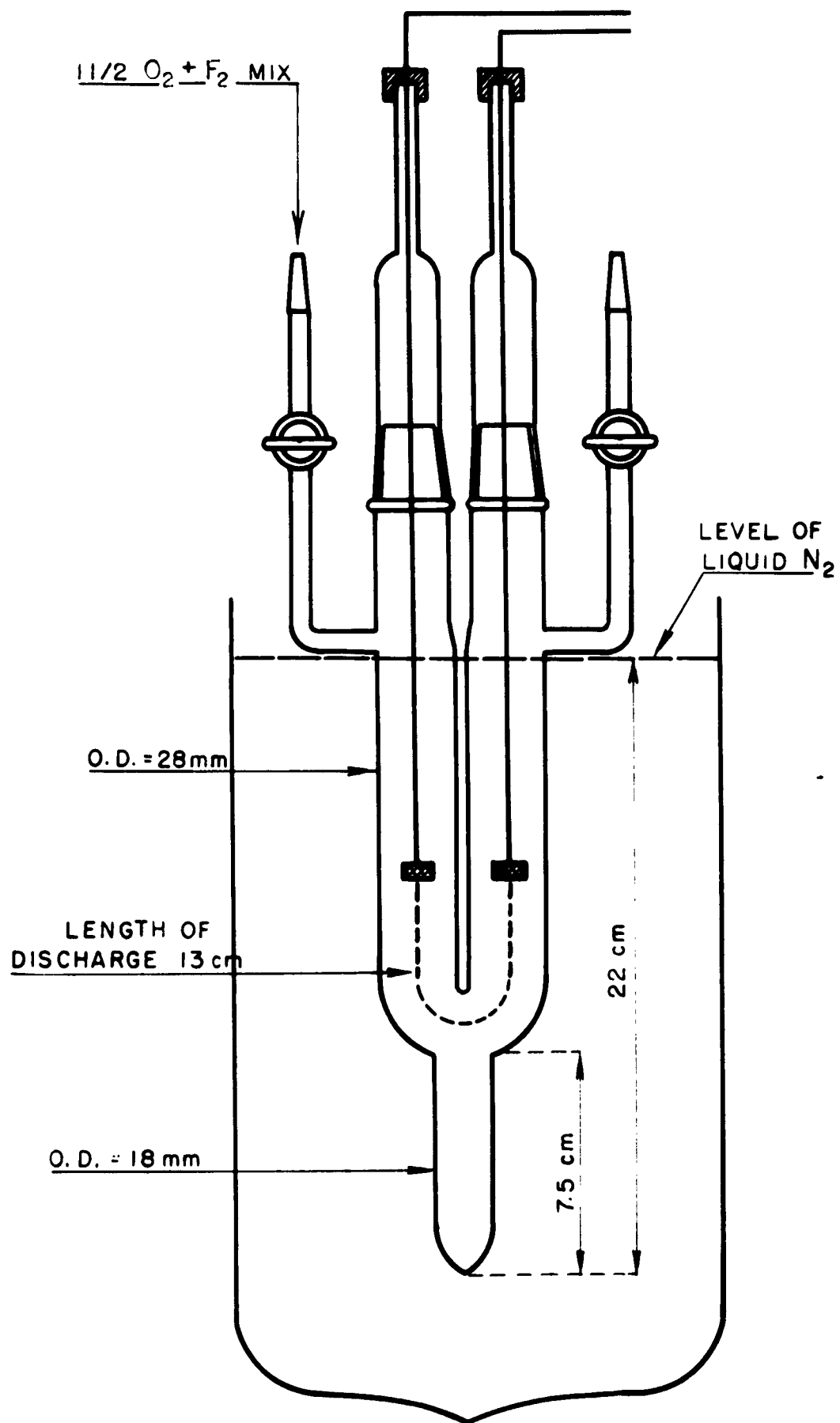
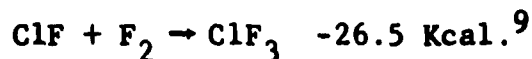


FIGURE 5.  
THE C-S APL DISCHARGE TUBE

It is known that at temperatures above 125°K., liquid ozone causes explosions with liquid O<sub>2</sub>F<sub>2</sub>. We avoided, therefore, mixing these compounds.

The traces of the unknown violet compound resemble the violet compound obtained from the O<sub>2</sub>F<sub>2</sub> + ClF reaction or from the reaction between O<sub>2</sub> and ClF<sub>3</sub> under ultraviolet light. If the formation of this violet product is due to the presence of traces of chlorine-containing compounds, its nature would be the same as that of our violet product obtained in the O<sub>2</sub>F<sub>2</sub> + ClF reaction. To investigate this possibility, experiments were performed with O<sub>2</sub> + F<sub>2</sub> + ClF mixtures.

Attempts were made to synthesize the violet compound directly from a gaseous mixture of O<sub>2</sub> + F<sub>2</sub> + ClF, by passing an electrical discharge. A U-shape reaction tube, shown in Fig. 3 was used. To avoid a possible explosion if the reaction



took place, only 3.3 vol.% ClF was added to the 1:1 oxygen-fluorine mixture. The gaseous O<sub>2</sub> + F<sub>2</sub> + ClF mixture was fed into the reaction vessel cooled in a liquid oxygen or liquid nitrogen bath. There was no difference in the results obtained at 90° and 77°K. An electrical discharge of 15-25 mA, 2000-3000V., was sent through the mixture at a pressure of 12 ± 5 mm Hg.

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(9) Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, Supplement II, Part 1, Longmans, Green and Co., London, New York, Toronto, 1956.

Dioxygen difluoride and some trioxygen difluoride were formed as a precipitate on the walls of the cooled part of the U-tube between the electrodes. In addition, a grey-blue deposit (most probably ozone) appeared on the walls of the inlet side of the tube above the electrode. Some unreacted ClF also deposited just above the grey-blue compound. However, no violet compound was formed.

When the temperature was increased to 120°K., the grey-blue deposit disappeared. The melted ClF flowed down and combined with the O<sub>2</sub>F<sub>2</sub> to form the violet compound (as in the usual O<sub>2</sub>F<sub>2</sub> + ClF reaction), and ClF<sub>3</sub>.

### VIII. REMARKS ON HYDROGEN SUPEROXIDE, $\text{H}_2\text{O}_4$

In the First Annual Progress Report for the Office of Naval Research, 1960, (pp. 34-43), the synthesis and the characteristics of hydrogen superoxide,  $\text{H}_2\text{O}_4$ , were described. Hydrogen superoxide was produced by the bombardment of  $\text{O}_3$  with hydrogen atoms at 77°K. The product obtained by us contained 52 wt.% of  $\text{H}_2\text{O}_4$ .

It is of interest that Zaslowsky, Martinez and Wojtowicz<sup>10</sup> of the Olin Mathieson Chemical Corporation have recently confirmed our findings and substantially increased the yield of  $\text{H}_2\text{O}_4$ . In nearly all their experiments, the molar ratio of oxygen to hydrogen peroxide is 1:1. This fact strongly supports the existence of a stoichiometric compound. The highest concentration obtained was 72 wt.%  $\text{H}_2\text{O}_4$  and 28 wt.%  $\text{H}_2\text{O}$ . Regardless of the interpretation the important fact is that substantial quantities of oxygen above the composition  $\text{H}_2\text{O}_2$  are introduced into the solid.

The above-named authors made the following statement:

"No explanation can be offered at the present time to account for the failure by Giguere and Chin<sup>11</sup> to detect the superoxide by the spectroscopic method."

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(10) Martinez, F., and Wojtowicz, J. A., "Study of Superoxides," AFOSR-105, Contract No. AF 29(600)-1667, OMCC-9038-GFR-1, Olin Mathieson Chem. Corp., New Haven, Conn., April, 1961.

(11) Giguere, P. A., and Chin, D., J. Chem. Phys., 31, 1685 (1959).



As we pointed out previously Giguere and Chin did not analyze their product for surplus oxygen content. Thus, it is not certain that they actually prepared  $\text{H}_2\text{O}_4$ .

Nekrasov, Skorohodov and Kobozev have emphasized<sup>12</sup> that Giguere and Chin<sup>11</sup> used solid, rather than liquid,  $\text{O}_3$ . In the opinion of the Soviet investigators, Giguere and Chin did not preclude the stabilization of the  $\text{HO}_2$  radical by diffusion into the liquid  $\text{O}_3$ , but on the contrary increased its reduction by atomic hydrogen to  $\text{H}_2\text{O}_2$ .

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(12) Nekrasov, L. I., Skorohodov, I. I., and Kobozev, N. I., Zhurnal Fiz. Khim., 35, 691-693 (1961).

**APPENDIX**

## THE REAGENTS USED

Dioxygen difluoride,  $O_2F_2$ , was prepared directly from the elements, essentially by the method described by Ruff and Menzel<sup>1</sup> and by Aoyama and Sakuraba.<sup>2</sup> The flow diagram for our modified apparatus is shown in Fig. A-1. The 1:1 gaseous mixture of fluorine and oxygen is prepared in the perfluorinated stainless-steel cylinder. The cylinder has a volume of about 8 l. and is used at pressures up to 80 p.s.i.a. The  $O_2-F_2$  mixture is fed from this cylinder through the flowmeter containing Kel-F oil, through the trap cooled with liquid oxygen to eliminate impurities condensable at this temperature and into the reaction vessel. The reaction vessel 6.5 cm. in diameter and 18 cm. long, is made of Pyrex glass; it is cooled to 77 or 90°K. A detailed sketch of the reaction vessel is shown in Fig. A-2.

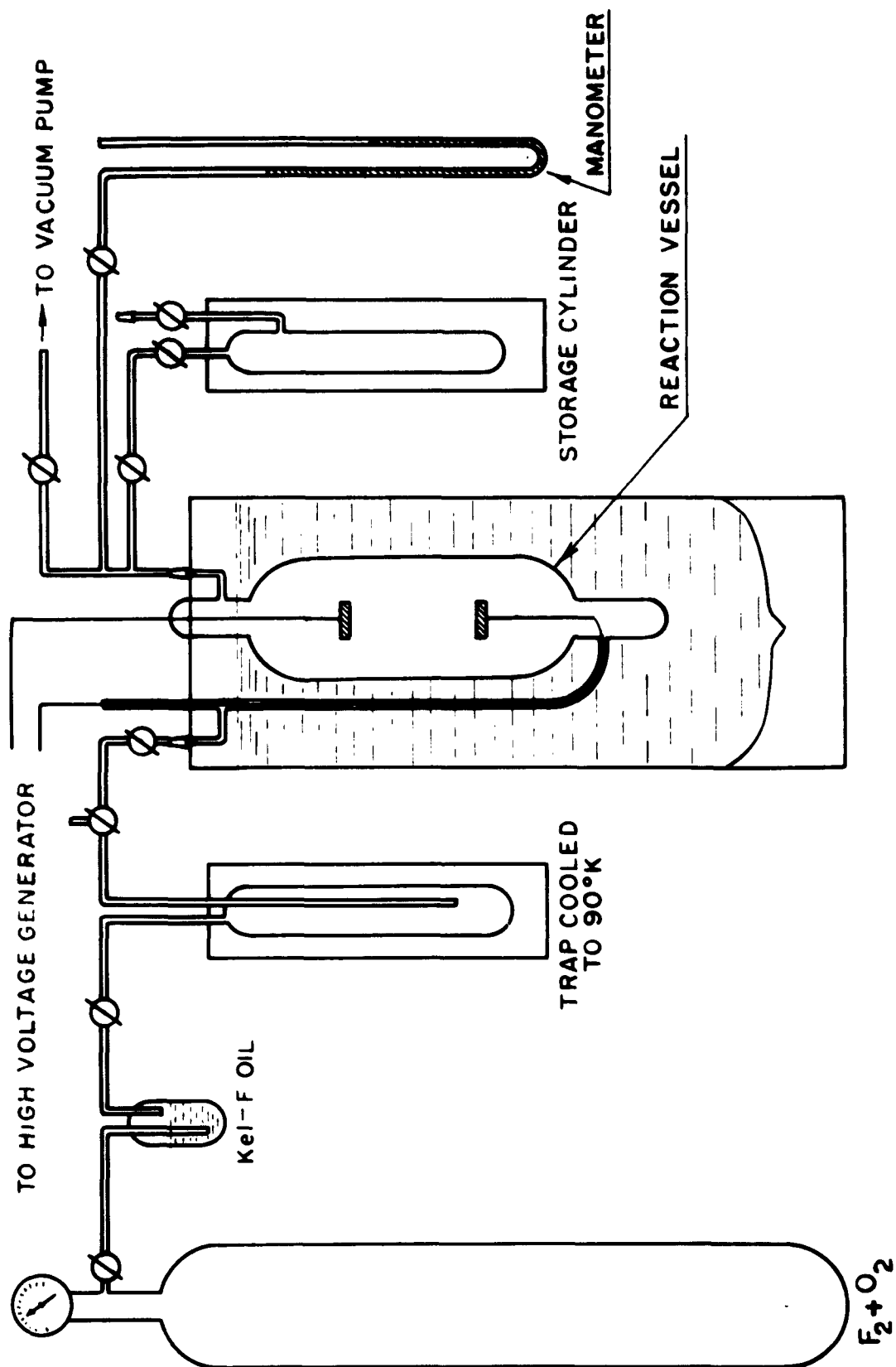
A high-voltage electrical discharge is established in the reaction vessel between two copper electrodes, which are fixed 10-cm. apart. The electrodes are 2 cm. in diameter and are connected to copper wires sealed into the reaction vessel by Teflon plugs. The other plugs in the system have ground-glass joints that are

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(1) Ruff, O., and Menzel, W., Z. anorg. allgem. Chem., 211, 204 (1933).

(2) Aoyama, S., and Sakuraba, S., J. Chem. Soc. Japan, 59, 1321 (1938).

FIGURE 3. Schematic Diagram of the Apparatus for the Preparation of  $\text{OF}_4$



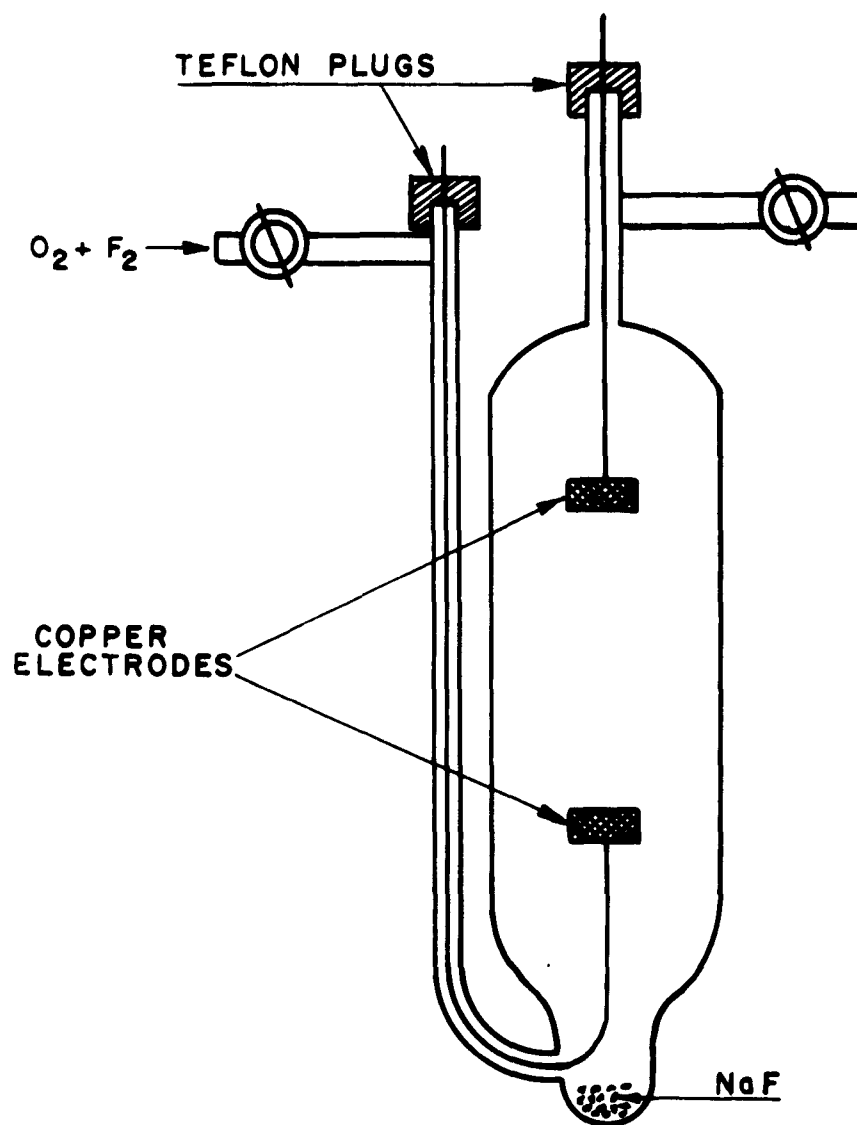


FIGURE A-1.

REACTION VESSEL FOR PREPARATION OF  $\text{OF}_2$ .

lubricated with Kel-F grease. The discharge varies from 25 to 30 ma. at 2100-2400V. The flow of the  $F_2$ - $O_2$  mixture is adjustable so that the pressure in the reaction vessel is maintained at  $12 \pm 5$  mm. Hg.

The electrical part of the apparatus consists of a 110-5000V. 60-cycle, single-phase transformer, in series with a 1000-ohm Ohmite vitreous enameled limiting resistor, together with a 0-100 milliammeter and a 0-5000 voltmeter.

The formation of dioxygen difluoride consumes all the entering  $F_2$ - $O_2$  mixture. The product condenses in solid form on the walls of the reaction vessel. When the preparation is completed, the electrical discharge and the gas supply are stopped, the reaction vessel is warmed to dry-ice temperature and the  $O_2F_2$  is distilled into the storage cylinder cooled in a liquid-nitrogen bath. Distillation is conducted at reduced pressure; all the connecting tubes must be cooled with dry ice. Some  $O_2F_2$  may decompose upon distillation. Therefore, the  $O_2$  and  $F_2$  formed must be pumped off while the  $O_2F_2$  is cooled with liquid nitrogen.

Sodium fluoride, NaF pellets (ignited) are placed into the reaction and storage vessels, in order to remove any HF and  $SiF_4$  which may have formed. NaF combines with these compounds according to the equations:



Pure dioxygen difluoride can be stored for extended periods of time in Pyrex glass cylinders cooled to 90°K.

Trioxxygen difluoride,  $\text{O}_3\text{F}_2$ , was prepared by a method similar to that used for preparing  $\text{O}_2\text{F}_2$ . The gaseous  $\text{F}_2$ - $\text{O}_2$  mixture must contain three volumes of  $\text{O}_2$  and two volumes of  $\text{F}_2$ . This mixture is found to combine quantitatively to form  $\text{O}_3\text{F}_2$  in the same type of apparatus that is used for  $\text{O}_2\text{F}_2$  preparation.<sup>3,4,5</sup> The construction of the reaction vessel is slightly different, as is shown in Fig. A-3. Slightly different also are the reaction conditions: the reaction vessel is cooled in a liquid-nitrogen bath, and the electrical discharge varies from 20 to 35 ma. at 2000-2200V. The gas pressure in the reaction vessel is the same, i.e.,  $12 \pm 5$  mm. Hg.

When the preparation is completed, the gas flow and the discharge are stopped and the reaction vessel is warmed to 90°K. by changing to a liquid-oxygen bath. Trioxxygen difluoride liquefies

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- (3) Kirshenbaum, A. D., Aston, J. G., and Grosse, A. V., Final Report, Contract No. DA-36-034-ORD-2250, Research Institute of Temple University, Nov. 18, 1958.
  - (4) Kirshenbaum, A. D., and Grosse, A. V., J. Am. Chem. Soc., 81, 1277 (1959).
  - (5) Kirshenbaum, A. D., Grosse, A. V., and Aston, J. G., J. Am. Chem. Soc., 81, 6398 (1959).

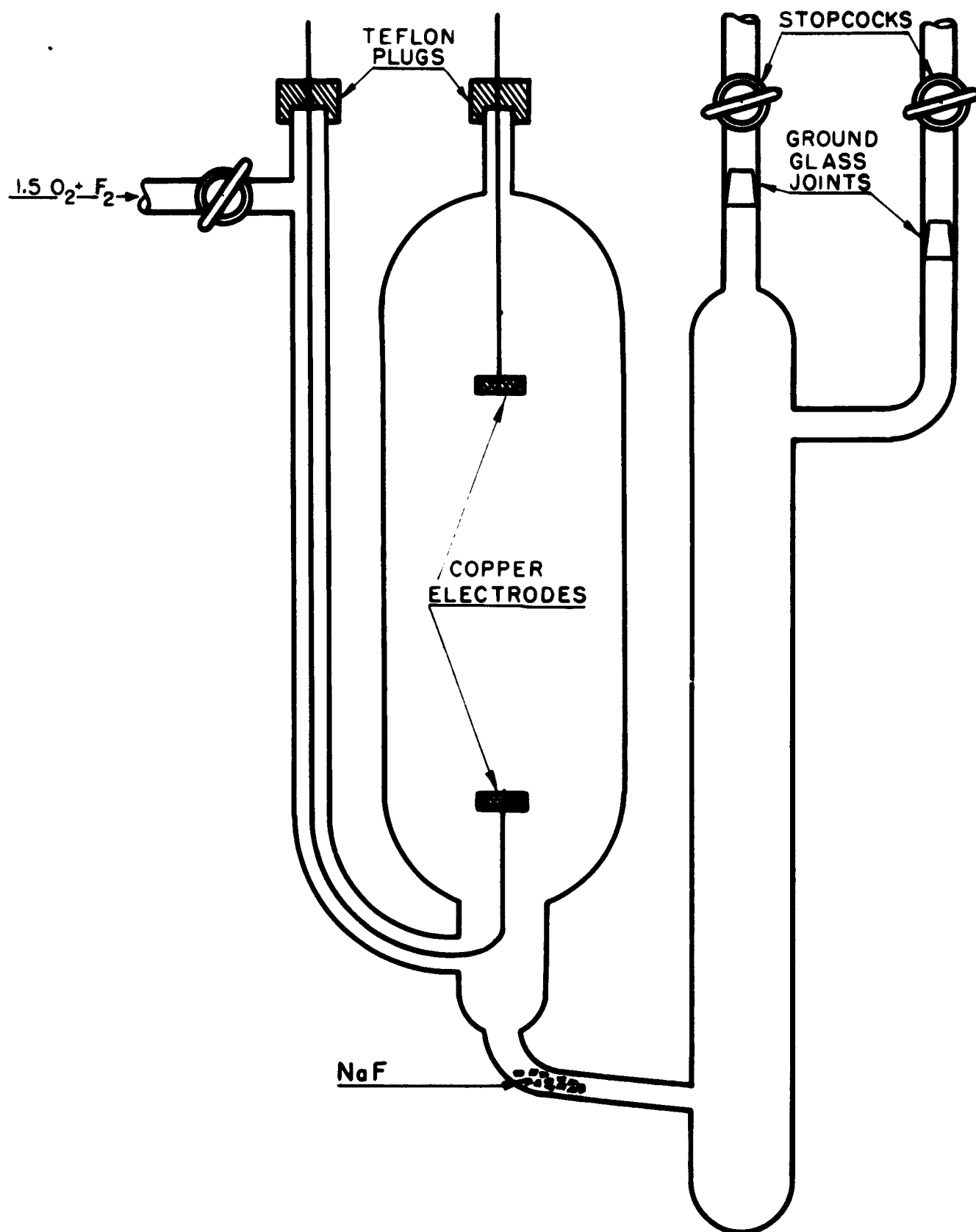
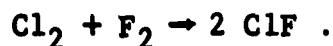


FIGURE A-3.  
REACTION VESSEL FOR PREPARATION OF  $O_2F_2$



and flows into the side tube. This tube is then disconnected and can be used as the storage vessel. Pure trioxxygen difluoride can be stored for a long time at 77°K. in Pyrex-glass vessels. The rate of decomposition at this temperature is about  $3.6 \times 10^{-5}$ /hr.

Chlorine monofluoride, ClF, was prepared in our laboratories from gaseous Cl<sub>2</sub> and F<sub>2</sub><sup>6,7</sup> in accordance with the reaction:



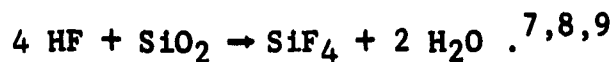
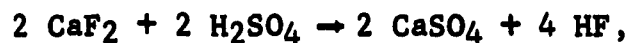
About 250 cm<sup>3</sup>/min. of each gaseous Cl<sub>2</sub> and F<sub>2</sub> were passed through a stainless-steel tube, vol. 56 cm<sup>3</sup>, at 400-500°C. The residence time was about 7 sec. The product was passed through a trap cooled with dry ice to remove ClF<sub>3</sub>, if formed in small amounts, or excess of free Cl<sub>2</sub>, if present, and into a second trap cooled with liquid oxygen, where ClF was condensed. The apparatus was made of Kel-F traps, stainless-steel valves and copper tubing. The product was purified by distillation and contained over 99% ClF.

Silicon tetrafluoride, SiF<sub>4</sub>, was prepared according to the reactions:

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(6) Ruff, O., Ascher, E., and Laas, F., Z. anorg. allgem. Chem., 176, 256 (1928).

(7) Brauer, Georg, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, 1954.

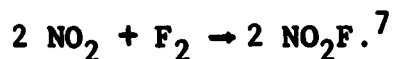


The mixture of  $\text{CaF}_2$ ,  $\text{SiO}_2$  and  $\text{H}_2\text{SO}_4$  was warmed slightly in a glass flask, and the gas formed was passed through two traps cooled with dry ice (to separate the possible excess of HF) into a glass trap cooled with liquid  $\text{O}_2$ , where  $\text{SiF}_4$  was condensed. The product was purified by sublimation.

Phosphorus trifluoride,  $\text{PF}_3$ , was prepared according to the reaction:



Nitryl fluoride,  $\text{NO}_2\text{F}$ , was prepared in our laboratories according to the equation:



All other reagents were the commercial products of the highest available purity as supplied by Stauffer Chemical Co., General Chemical Division of Allied Chemical Co., Pennsalt Chemicals Corp., E. I. du Pont de Nemours and Co., Matheson Co., Air Reduction Co. and others.

Most of these reagents were further purified by fractional distillation.

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(8) Lebouche, L., Fischer, W., and Biltz, W., Z. anorg. allgem. Chem., 207, 64 (1932).

(9) Ruff, O., and Ascher, E., Z. anorg. allgem. Chem., 196, 413 (1931).